TENNESSEE VALLEY AUTHORITY
Public Power Institute

Chemical Fixation of CO_2 in Coal Combustion Products and Recycling Through Biosystems

Annual Technical Progress Report

DE-FC26-00NT40933

00RE6-266797

December 10, 2002

Chemical Fixation of CO_2 in Coal Combustion Products and Recycling Through Biosystems

Annual Technical Progress Report

Reporting Period Start Date: October 1, 2001

Reporting Period End Date: September 30, 2002

C. Henry Copeland, Paul Pier, Samantha Whitehead, and David Behel

December 10, 2002

DE-FC26-00NT40933

00RE6-266797

Tennessee Valley Authority (TVA)
P.O. Box 1010
Muscle Shoals, Alabama 35662-1010

ABSTRACT

This Annual Technical Progress Report presents the principal results in enhanced growth of algae using coal combustion products as a catalyst to increase bicarbonate levels in solution. Optimal production of biomass depends on a number of factors. These factors include pH management, harvesting, and impact of auxiliary operations on the algae population. A number of experiments are presented which attempt to identify and characterize the impact of these factors.

NETL F 510.1-5#

(12/1999) OPI=PS10
(Previous Editions Obsolete)

REQUEST FOR PATENT CLEARANCE FOR RELEASE OF CONTRACTED RESEARCH DOCUMENTS

TO: ☐ For Technical Reports
AAD Document Control
MS F07
U.S. Department of Energy - NETL
P.O. Box 880
Morgantown, WV 26507-0880

♦Contract Agreement No.
DE-FC26-00NT40933

Name & Phone No. of DOE COR

☒ For Technical Reports
AAD Document Control
MS 921-143
U.S. Department of Energy - NETL
P.O. Box 10940
Pittsburgh, PA 15236-0940

☐ For Technical Papers/Journal Articles/Presentations
Mark P. Dvorscak
U.S. Department of Energy
9800 S. Cass Avenue
Argonne, IL 60439
FAX: (630) 252-2779

A. CONTRACTOR ACTION (CONTRACTOR COMPLETES PART A. 1-5)

1. Document Title: Chemical Fixation of CO_2 in Coal Combustion Products and Recycling Through Biosystems

2. Type of Document: X Technical Progress Report ☐ Topical Report ☐ Final Technical Report
☐ Abstract ☐ Technical Paper ☐ Journal Article ☐ Conference Presentation
☐ Other (please specify):

3. Date clearance needed:

♦4. Patent information.

Yes	No	
X	☐	Is any patentable subject matter disclosed in the report?
X	☐	If so, has an invention disclosure been submitted to DOE Patent Counsel? If yes, identify disclosure number or DOE Case Number S-97,010
☐	X	Are there any patent-related objections to the release of this report? If so, state the objections.

♦5. Signed G Henry Copeland Tennessee Valley Authority Date 12/13/2002

Name & Phone No. C. Henry Copeland, (256) 386-3762

Address
CTR T101A 1K-M
P. O. Box 1010
Muscle Shoals, AL 35662-1010

B. DOE PATENT COUNSEL ACTION

☐ Patent clearance for release of the above-identified document is granted.
☐ Other: _____

Signed Date
(Patent Attorney)

♦ Must be completed by the contractor.

CONTENTS

FIGURES

TABLES

1.0 Introduction

Algal growth can be limited by several factors, including the level of bicarbonate available for photosynthesis, the pH of the growth solution, and the size of the cell population, which determines the available space for additional growth. Fly ash has been demonstrated to increase the available CO_2 in solution above the limits that are achievable with dissolved gas alone, in order to supply additional CO_2 to increase photosynthesis and algal biomass production. The amount of dissolved CO_2 can be used to control pH for optimum growth. Periodic harvesting of algae can be used to maintain algae in the exponential rapid phase of growth. The following experiments were undertaken to determine the CO_2 addition, pH range, and harvesting method that would provide optimum algal biomass production using the CO_2/fly ash reactor described in the appendix of the Technical Progress Report DE-FC26-00NT40933, 00RE6-266797: "Conversion of Carbon Dioxide Gas to Carbonate Solution Using Fly Ash as a Catalyst."

2.0 MicroAlgae Culture

2.1 Preparation

Initially, three species of microalgae were obtained as disc cultures (MICRO ALGAE DISKS®, Florida Aqua Farms, Inc., Dade City, Florida) and prepared according to manufacturer instructions. Isochrysis, Tetraselmis, and Nannochloropsis were cultured in 1-liter (L) glass jars, and then transferred to 5-gallon glass carboys. An artificial seawater medium was used (Instant Ocean and deionized water, prepared according to product labeling). Cultures were aerated with air stones and placed under grow lights. The carboy cultures were used as stock for cultures used in algae growth experiments. For experiments, normally four to eight liters of the carboy stock culture were added to a five-gallon aquarium and brought to 16 liters final volume with artificial seawater.

In the months following the initial growth experiments, the three stock cultures commingled and Tetraselmis began to predominate. For fiscal year 2002 experiments, Tetraselmis was the predominant species in laboratory cultures.

2.2 Stock Culture Maintenance

Cultures were diluted on a regular basis to maintain an active cell population. Nutrients (Kent Marine Pro-Culture F/2 Nutrient Solutions Parts A & B, obtained from Aquatic Ecosystems, Apopka, FL) were added weekly according to manufacturer instructions, and fresh deionized water was added to aquariums to make up for evaporative losses.

2.3 Microscopic Evaluation and Enumeration of Cells

During the experiments, aquariums were sampled regularly to check for contamination and enumeration of cells. Algae cells were counted under 100x

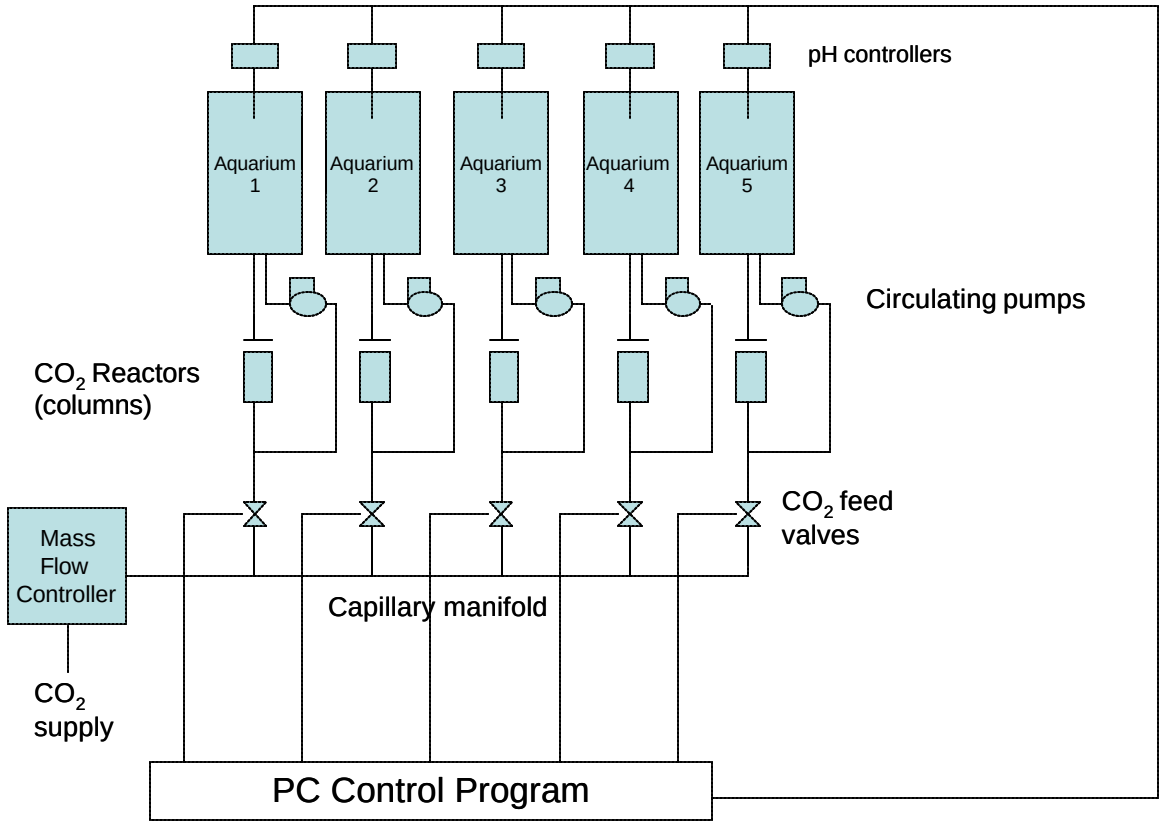
magnification using a hemacytometer, according to the method described in Plankton Culture Manual (Hoff and Snell, ISBN: 09662960-0-1, Florida Aqua Farms).

Contamination of cultures with an unidentified filamentous macroalgae became evident as Experiments 4 and 5 progressed.

3.0 CO_2 and pH Control System

In order to assess the effect of CO_2 additions and subsequent pH changes on algal growth, a CO_2/pH control system was implemented (Figure 1). The control system maintained the desired pH in each aquarium by monitoring pH levels, and opening and closing CO_2 supply valves as needed to increase and decrease the pH. A pH controller in each aquarium monitored the pH level. When no CO_2 was being supplied to the aquarium, the pH increased due to depletion of CO_2 in solution from algal photosynthesis. When the pH reached the desired upper limit, the CO_2 feed valve was opened, supplying CO_2 to the reactor water stream, which was continually circulated from the aquarium, through the CO_2 reactor, and back into the aquarium. When the pH in the aquarium decreased to the lower limit, the CO_2 supply to the water stream was discontinued.

Figure 1
Algal Biosystem pH Control System



A set of experiments was conducted to determine if the pH control system was functioning properly, and to determine optimum pH for the culture of marine phytoplankton. The pH levels were controlled in 0.2 increments for Experiments 1 through 4 (Table 1).

Table 1
pH Treatment Ranges for
Experiments 1–4

pH 7.8–8.0
pH 7.6–7.8
pH 7.2–7.4
pH 7.0–7.2

4.0 Experiment 1

4.1 Experimental

Aquariums were prepared using carboy stock solutions as described above in Section 2.1 Preparation, and the pH levels were controlled as described above in Section 3.0 CO_2 and pH Control System. Due to an error in the data collection program, pH data was not available for this experiment.

To assess algal regrowth with daily harvesting, and also to obtain a daily estimate of total algal biomass, two liters were harvested each day from the 16-liter volume in each aquarium. Two 200-mL aliquots were taken from the 2-liter sample and centrifuged at 10,000 rpm for 10 minutes. The resulting pellets were re-suspended with deionized water and centrifuged once more at 10,000 rpm. The pellets were combined and quantitatively transferred to a tared aluminum weighing pan and dried. In addition to algae, the pellets contained fly ash that had washed out of the column into the aquarium, so the sample was then ashed to a constant weight to determine the percent biomass, or algae, of the total pellet weight. The remainder of the 2-liter sample (~1600 mL) was vacuum-filtered through tared 24-cm Whatman #3 paper, and the filter papers were dried in an oven to a constant weight. The water from the centrifugation and filtering procedures was recovered and returned to the respective aquariums in order to maintain the proper volumes.

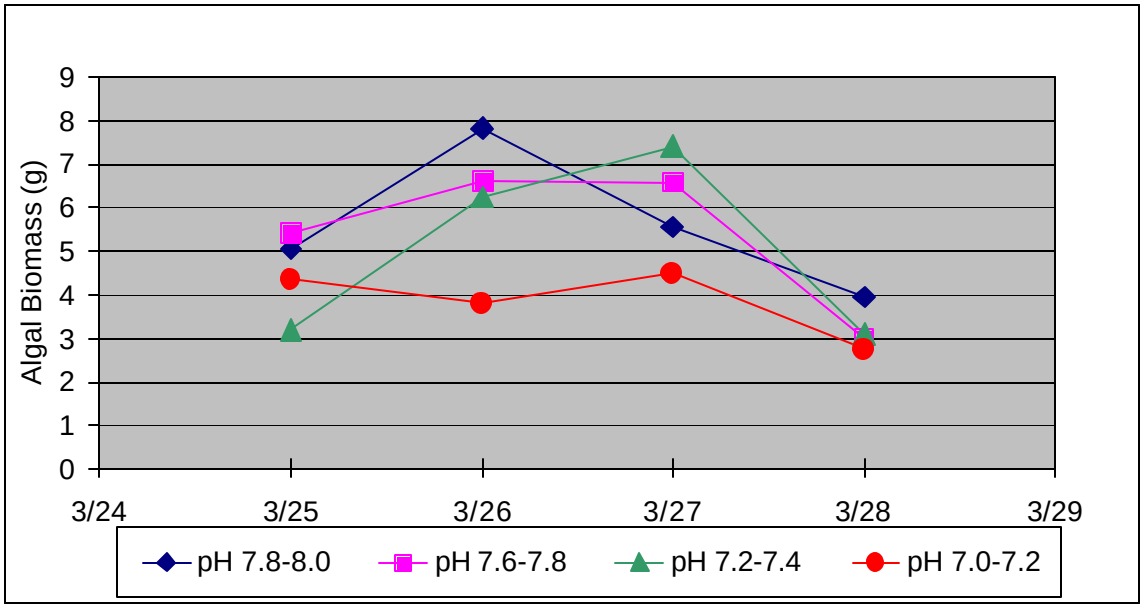
To obtain an estimation of total biomass in each aquarium, the biomass of the two 200-mL aliquots plus the biomass of the filtered 1600-mL fraction were combined, with the filtered fraction being corrected for ash using the ash content of that day's centrifuged pan sample. The biomass of this 2-L sample was then used to estimate the biomass of the total 16-L volume in the aquarium.

4.2 Results

Results from Experiment 1 are present in Figure 2. Total algal biomass in the microcosms during the course of the experiment was similar for all pH treatments

except pH 7.0–7.2. For pH 7.0–7.2, the biomass varied between 3.8 and 4.5 grams (g) before decreasing to 2.7 g at the final sampling point on 3/28. The remaining pH treatments, however, increased to between 6 and 8 g biomass during this time, before also decreasing to 3 to 4 g at the final sampling point on 3/28, similar to the biomass for the pH 7.0–7.2 treatment. These results indicate that the pH 7.0–7.2 treatment would not provide optimum growth conditions for algae, even though this treatment is receiving the highest amount of CO_2. Apparently the algae cannot take advantage of the high CO_2 provided, due to the reduction in growth from the effect of lower pH.

Figure 2
Experiment 1, Algal Biomass



5.0 Experiment 2

5.1 Experimental

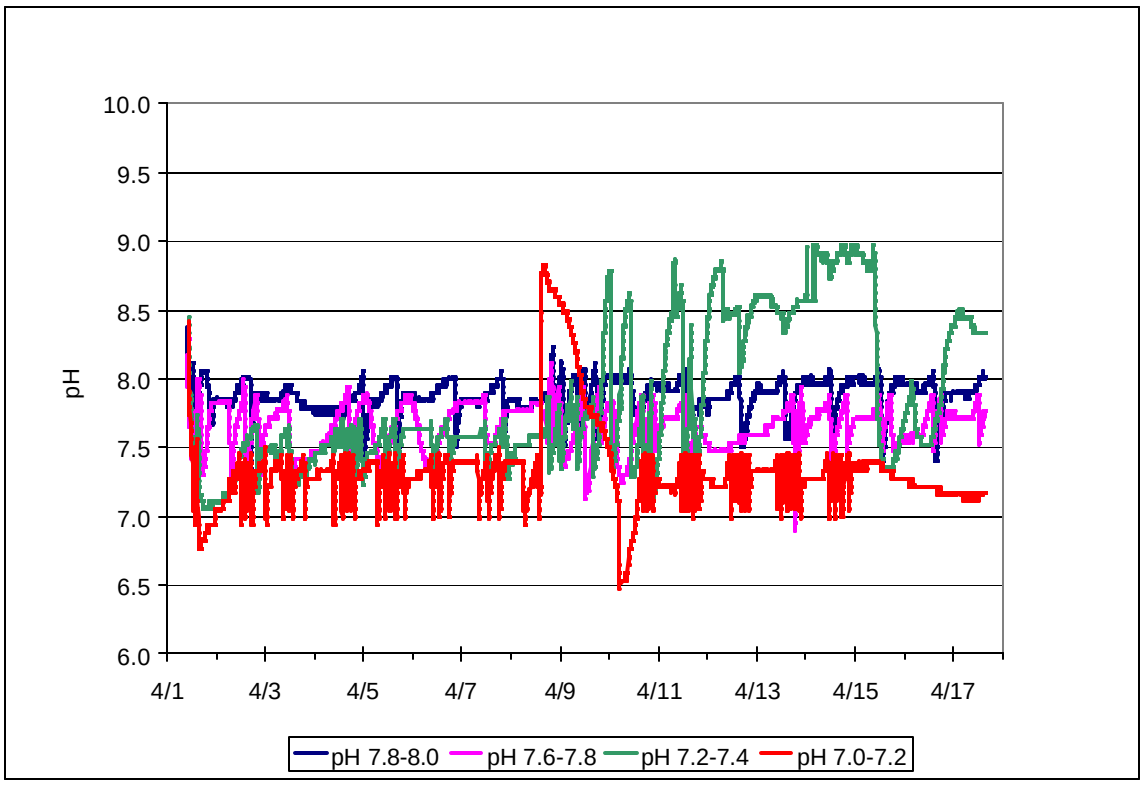
Based on the decreasing algal biomass encountered after repeated harvesting during Experiment 1, Experiment 2 was designed to track cell population trends during CO_2 introduction without the influence of harvesting. Aquarium preparation and pH level control were the same as in Experiment 1, but no algal biomass was harvested for this experiment.

5.2 Results

The pH monitoring data is given in Figure 3. The pH ranges were controlled by the CO_2 additions. However, the pH ranges were greater than the 0.2 units desired, with ranges of 0.4 to 0.6 pH units, due to the dynamic nature of the system. The biological aspect of the system does not respond to pH control as a conventional chemical system would. Also, difficulties with the control system allowed the pH to

go higher than desired for the 7.0–7.2 pH treatment on 4/8 and for the 7.2–7.4 pH treatment from 4/10 to 4/15, before CO_2 additions brought the pH down to the proper level.

Figure 3
Experiment 2, pH



Initial cell populations for Experiment 2 were approximately 1 x 10^6 cells/mL (Figures 4-7). Treatments pH 7.6–7.8 and pH 7.2–7.4 attained the highest cell concentrations of 6.9 x 10^6 and 6.0 x 10^6 cells/mL, respectively, although these high cell counts occurred in only one sampling period. For the remaining sampling points in these treatments and for the other two pH treatments, the highest cells counts normally ranged between 2 x 10^6 and 3 x 10^6 cells/mL. The pH treatment 7.2–7.4 appeared to be the most beneficial for algal cell growth, with cell counts above 3 x 10^6 for several sampling points, in addition to the 6.0 x 10^6 cell count discussed above. These higher counts occurred with a relatively high CO_2 feed followed by a period of several low CO_2 feeds. The highest cell counts were also observed for pH 7.8–8.0 and pH 7.6–7.8 under these conditions. This suggests that supplying a large amount of CO_2, with little or no CO_2 for a period afterwards, may be effective in enhancing algal cell growth.

Figure 4
Experiment 2, pH 7.8–8.0

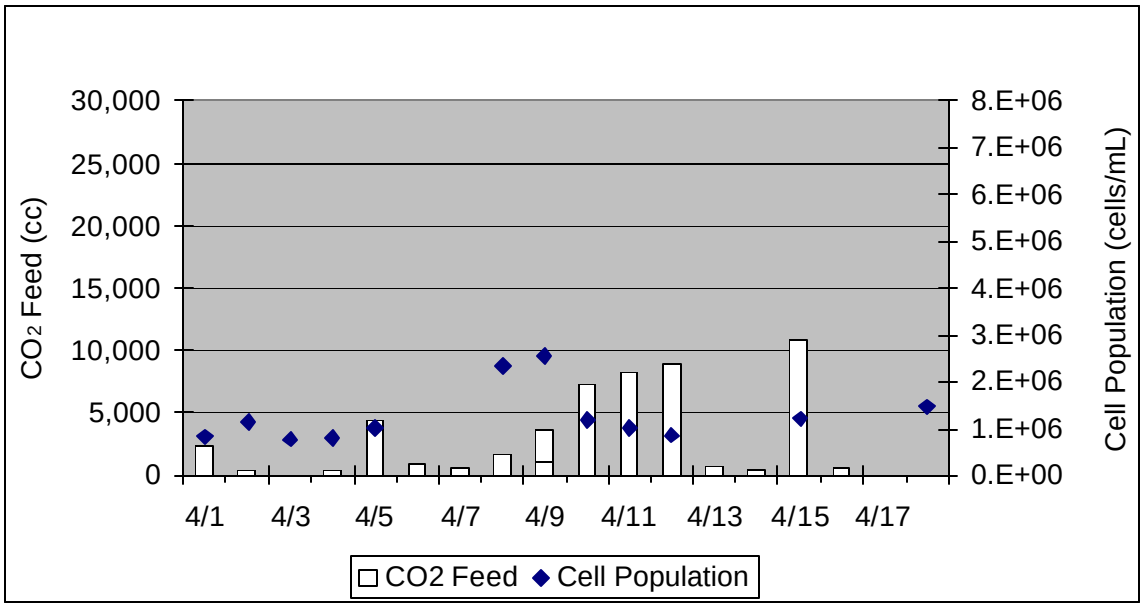


Figure 5
Experiment 2, pH 7.6–7.8

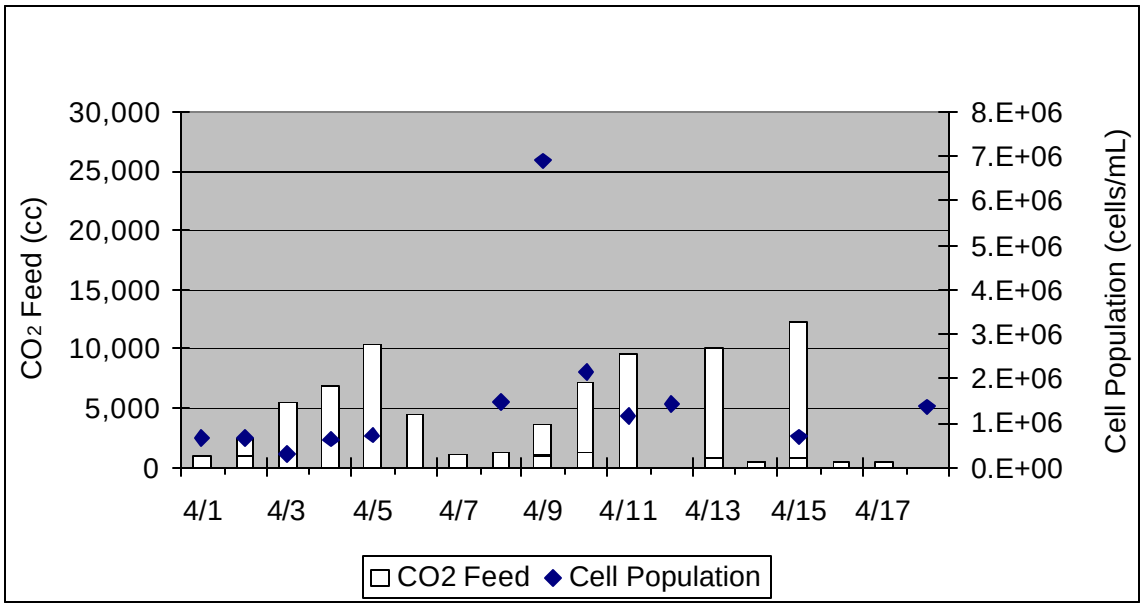


Figure 6
Experiment 2, pH 7.2–7.4

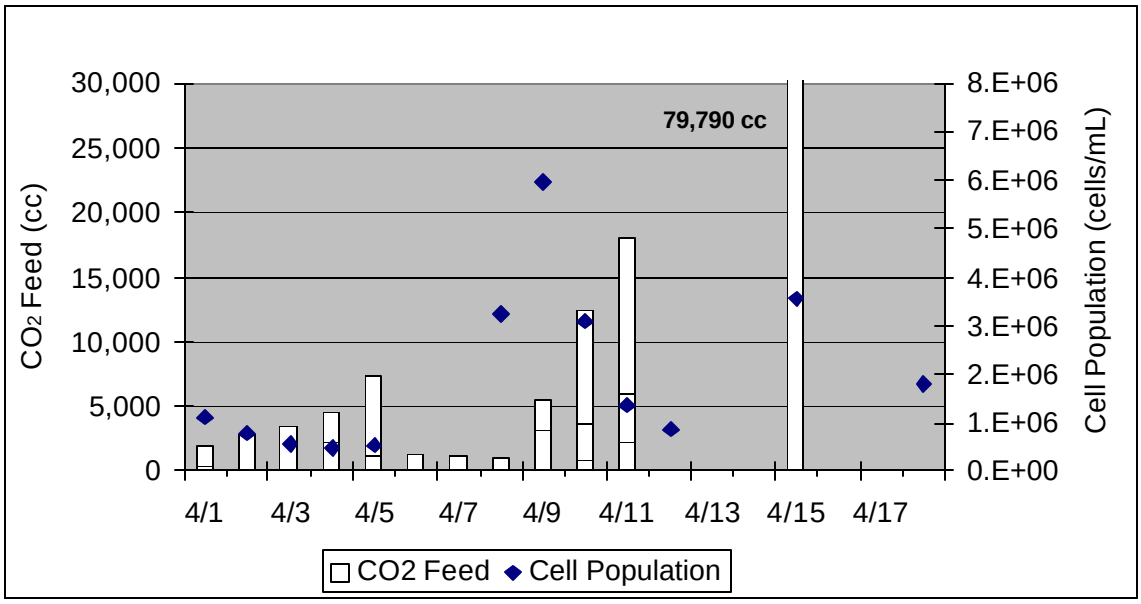
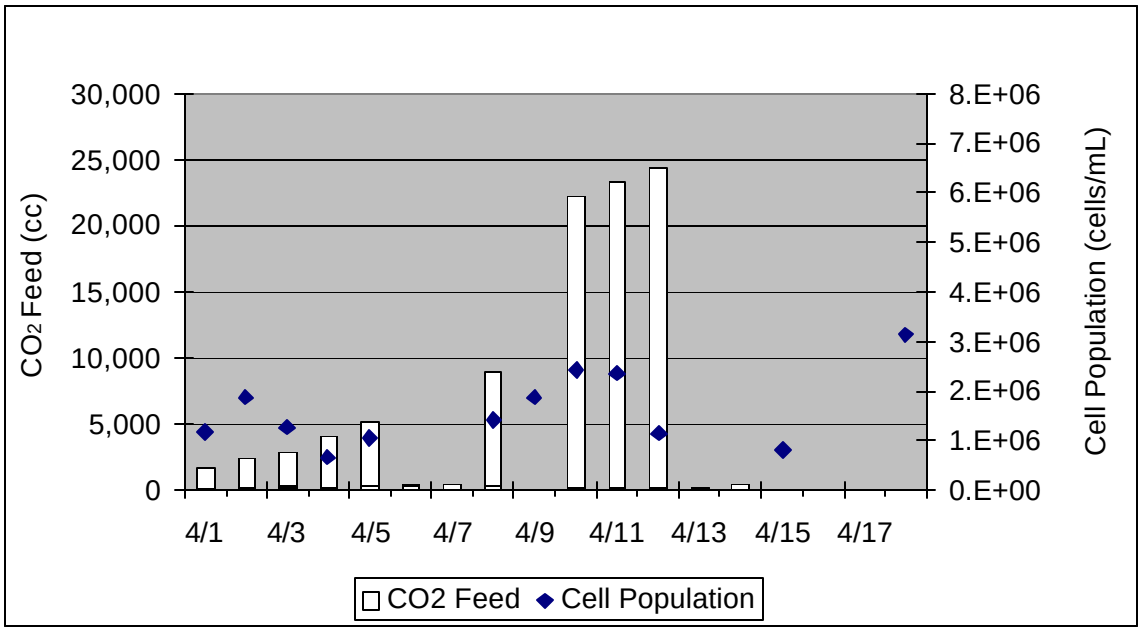


Figure 7
Experiment 2, pH 7.0–7.2



6.0 Experiment 3

6.1 Experimental

After observing the appearance of a film of algal biomass on the surface of the aquariums during the main growth phase in Experiments 1 and 2, the harvesting technique was modified to not remove a specific volume of algal suspension, but to periodically "skim" off this film and determine its biomass.

The pH was controlled by CO_2 addition to the algal biosystem, as in previous experiments. Skimmed harvesting samples were collected regularly, then transferred quantitatively to a tared aluminum weigh boat and dried to a constant weight. Samples were then ashed to a constant weight to determine actual biomass content.

6.2 Results

The pH varied outside the specified ranges, as shown in Figure 8. However, for the majority of the time, the pH was within the desired range, particularly for the 7.8–8.0 and 7.6–7.8 treatments, as indicated by periods on the plot in which the pH varied very little. The 7.4–7.6 and 7.0–7.2 treatments did not show as many of these stable pH periods, most likely because the addition of more CO_2 to maintain the lower pH levels caused greater fluctuations in pH.

The amount of algal biomass skimmed from the surface of the water is given in Figure 9. No pH treatment showed a consistent advantage over the others in enhancing biomass growth. The total biomass skimmed over the course of the experiment was also similar for the pH treatments (Table 2), with pH 7.6–7.8 slightly higher than the other treatments.

Figure 8
Experiment 3, pH

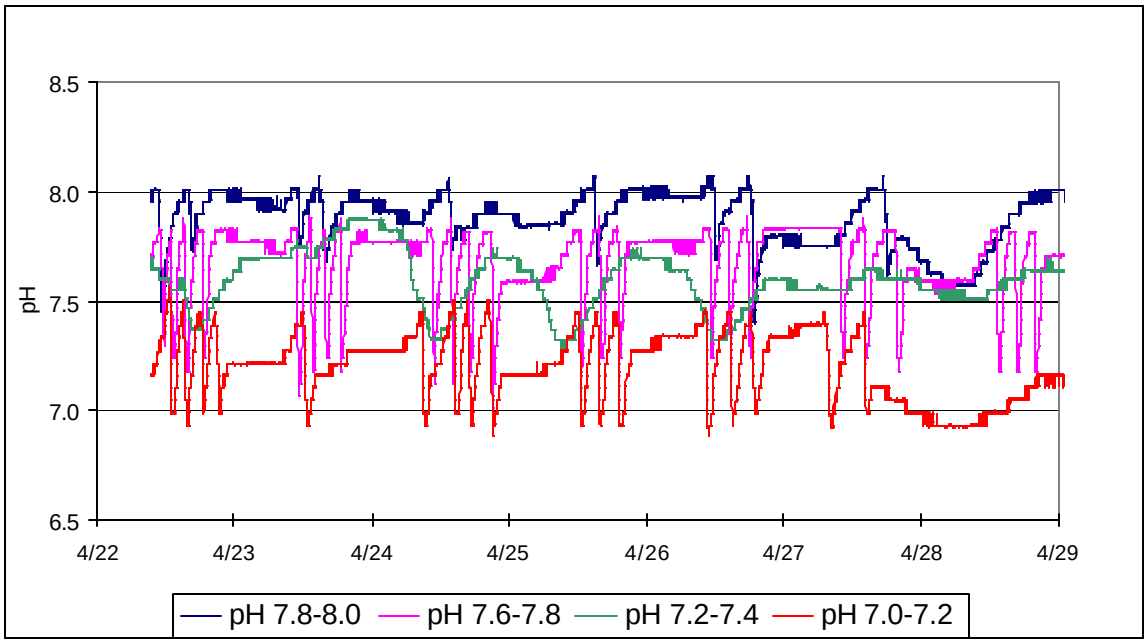


Figure 9
Experiment 3, Algal Biomass (Skimming Harvest)

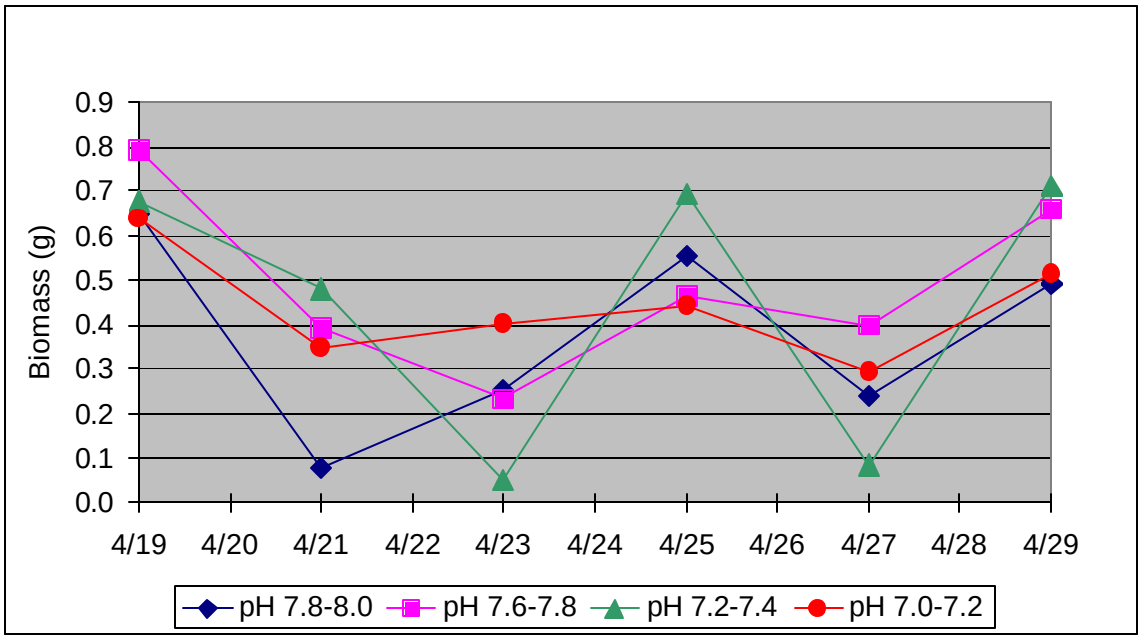


Table 2
Total Biomass Skimmed From Water Surface in Experiment 3

pH Treatment	Total Skimmed Biomass (g)
7.8–8.0	2.27
7.6–7.8	2.94
7.2–7.4	2.70
7.0–7.2	2.64

7.0 Experiment 4

7.1 Experimental

Harvesting technique and CO_2 additions were the same as in Experiment 3. A control aquarium without CO_2 addition to the biosystem was included in this experiment. At the completion of the experiment, all the algae from each aquarium were harvested by vacuum filtration to determine total biomass for each treatment.

7.2 Results

For the pH 7.2–7.4 treatment, initially the system was not provided with CO_2 due to a pump malfunction, which caused the pH to increase to 8.8 (Figure 10). A large amount of CO_2 was then put into the system, which brought the pH down to the desired range, and very little CO_2 was added after this to maintain the pH range.

After the large addition of CO_2 in the pH 7.2–7.4 treatment, cell counts increased steadily to a maximum of 2.2×10^6 cells/mL at the final measurement on 5/10, which was the highest cell population observed for the treatments (Figures 11-15). In addition, the total biomass harvested from the pH 7.2–7.4 treatment was 50% higher than the next highest biomass total (Table 3). Aquariums were skimmed only two times during the experiment, so the skimmed biomass has been included with the total biomass reported. These results suggested that allowing the algae to grow over a large pH range may be an effective method to increase biomass yield, similar to the results observed in Experiment 2. This could be accomplished by adding a relatively large amount of CO_2 that would decrease the pH by 0.5 to 1.0 units, followed by a period during which the reduction of CO_2/HCO_3 in solution due to algal photosynthesis would cause an increase back to the original pH, followed by another CO_2 addition. The subsequent Experiment 5 was designed to address this concept.

Figure 10
Experiment 4, pH

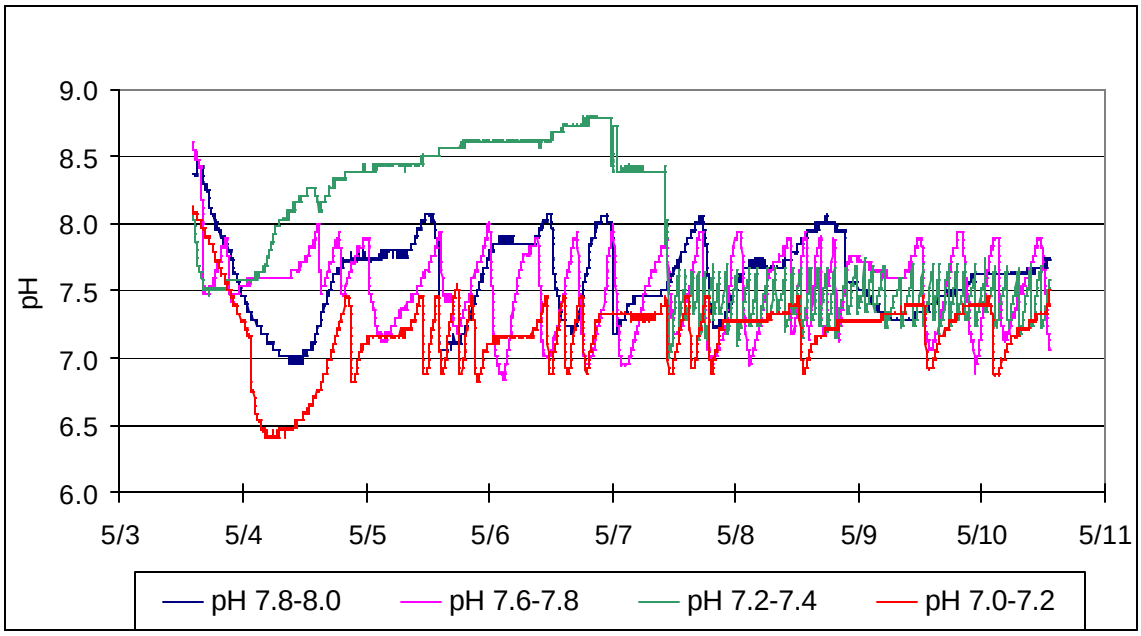


Figure 11
Experiment 4, pH 7.8–8.0

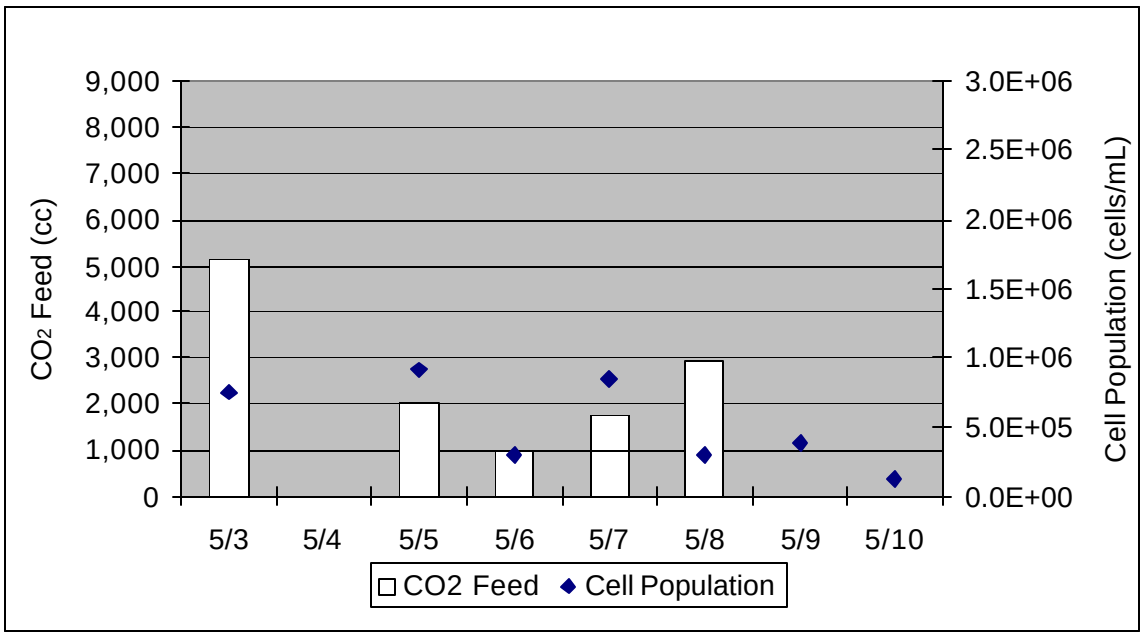


Figure 12
Experiment 4, pH 7.6–7.8

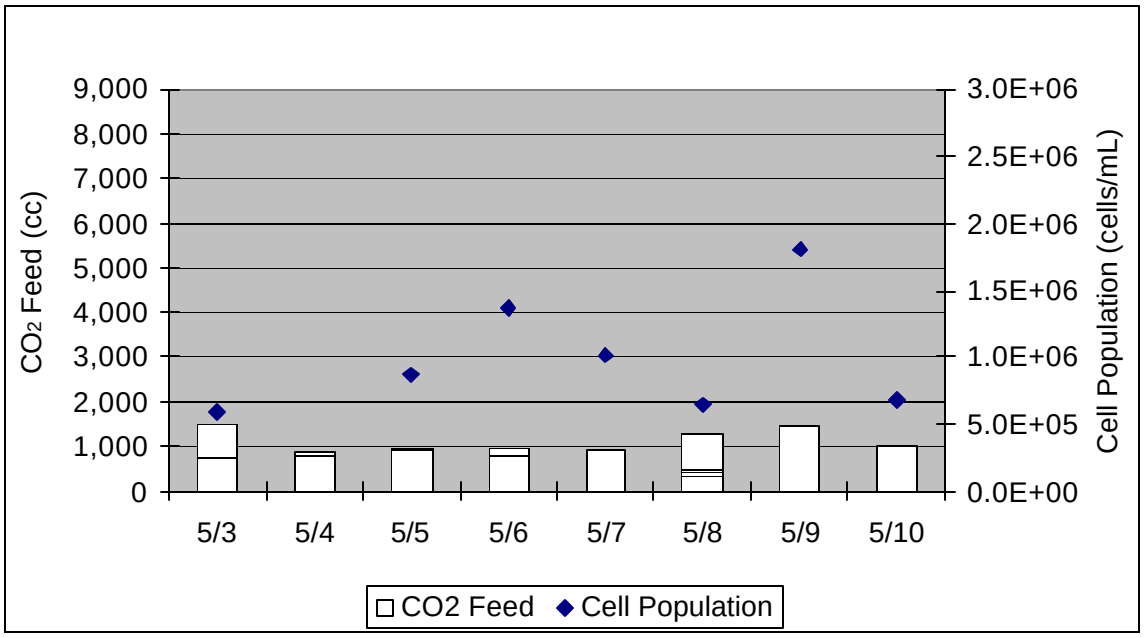


Figure 13
Experiment 4, pH 7.2–7.4

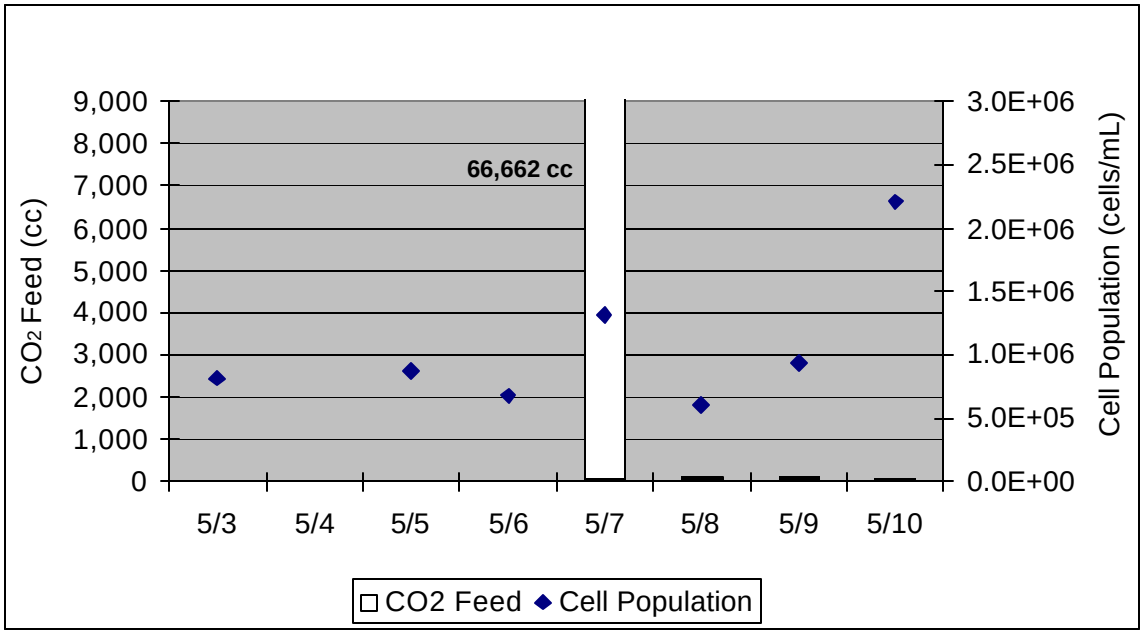


Figure 14
Experiment 4, pH 7.0–7.2

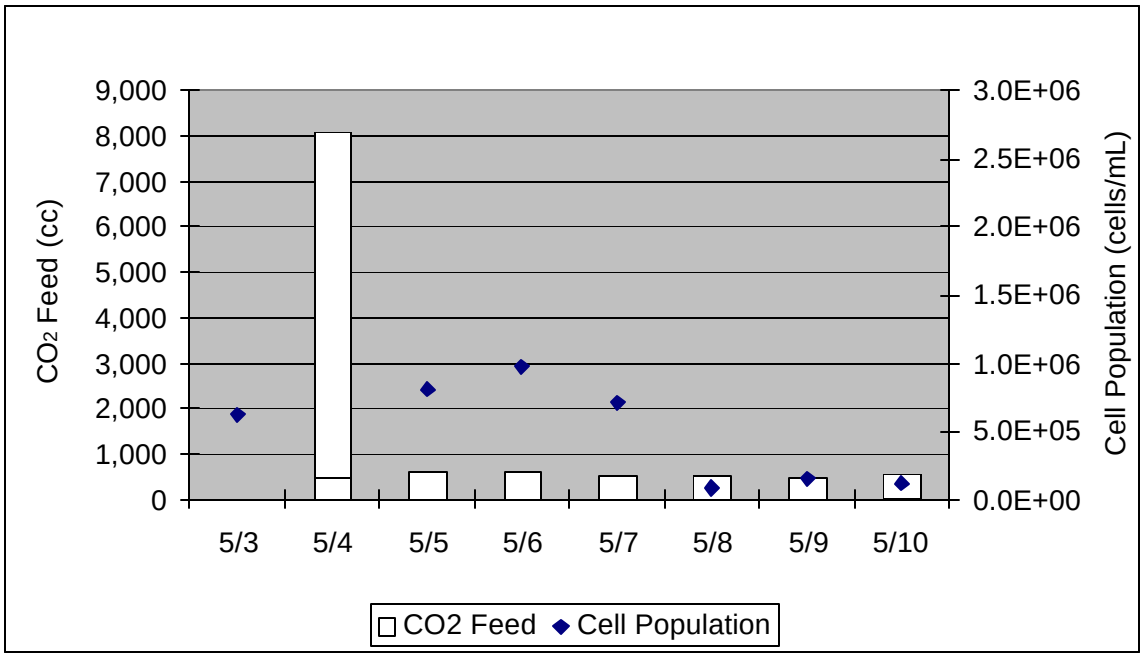


Figure 15
Experiment 4, Control Cell Population

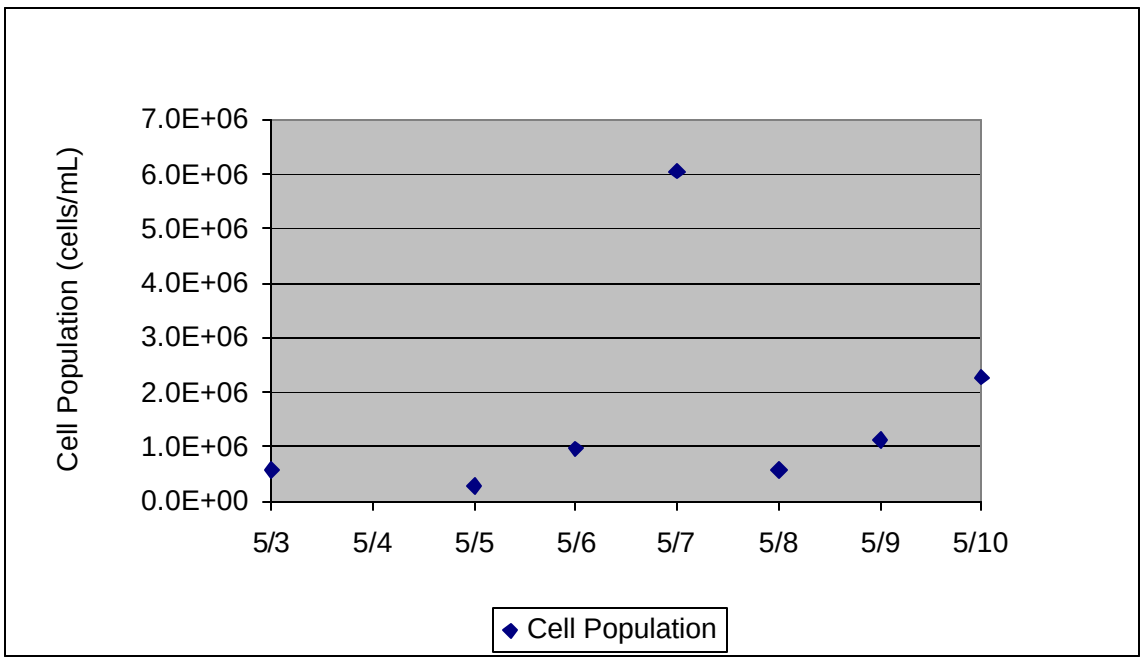


Table 3
Total Biomass for pH Treatments in Experiment 4

pH Treatment	Total Biomass Harvested* (g)
7.8–8.0	7.52
7.6–7.8	8.31
7.2–7.4	14.80
7.0–7.2	9.98
Control	8.21

* Total biomass refers to the total of daily skimming harvests plus the amount of biomass material filtered out of the aquarium after experiment completion.

8.0 Experiment 5

8.1 Experimental

Harvesting technique and CO_2 additions were the same as in Experiments 3 and 4. Expanded pH ranges were used in this experiment (Table 4).

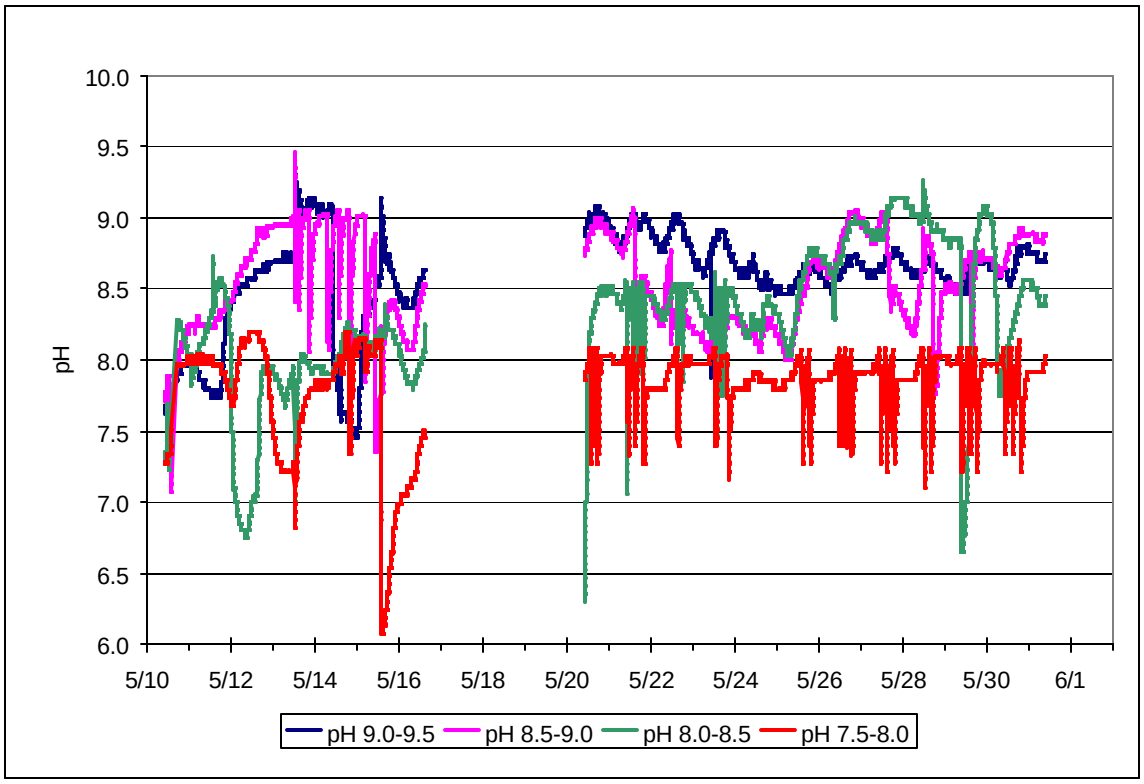
Table 4
pH Treatment Ranges for Experiment 5

pH 9.0–9.5
pH 8.5–9.0
pH 8.0–8.5
pH 7.5–8.0

8.2 Results

The pH controller/monitor data showed some difficulties with maintaining the proper pH ranges for the treatments (Figure 16). The pH 7.5–8.0 treatment maintained its range; however, the pH levels for 8.0–8.5 and 8.5–9.0 treatments were similar, with both ranging between a pH of 8.0 to 9.0. The pH 9.0–9.5 treatment did not reach its desired pH level, but stayed very consistently between pH 8.5 and 9.0. Only a small amount of CO_2 was added late in the experiment on and after 5/31 for this treatment, indicating that algal photosynthesis could not raise the pH above 9.0.

Figure 16
Experiment 5, pH



Cell populations were similar for the four pH treatments, with no treatment showing a consistent enhancement in cell numbers over the others (Figures 17-21). The pH 8.0–8.5 treatment had the highest total biomass of the four treatments, but was lower than the control biomass (Table 5). Algal cells in the control aquarium were not passed through a fly ash column and pump, and higher biomass in the control may have been due to the absence of the mechanical buffeting experienced by cells in the pH treatments. The total biomass for the pH 9.0-9.5 treatment had very little CO_2 added, but the algal cells were circulated through the pump and reactor column. Comparison of the total biomass for the pH 9.0-9.5 treatment with the control biomass shows that the control algal culture produced approximately two times the biomass of the pH 9.0-9.5 treatment. This difference may be due to the mechanical buffeting of the algal cells. Subsequent experiments will address methods to minimize or eliminate this problem.

Figure 17
Experiment 5, pH 9.0–9.5

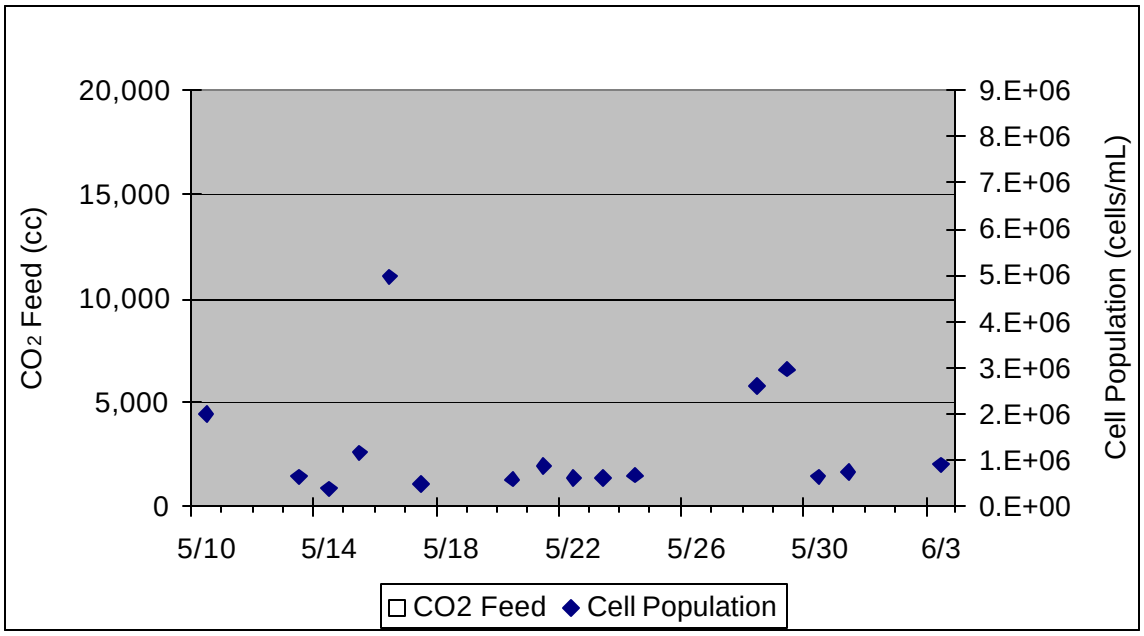


Figure 18
Experiment 5, pH 8.5–9.0

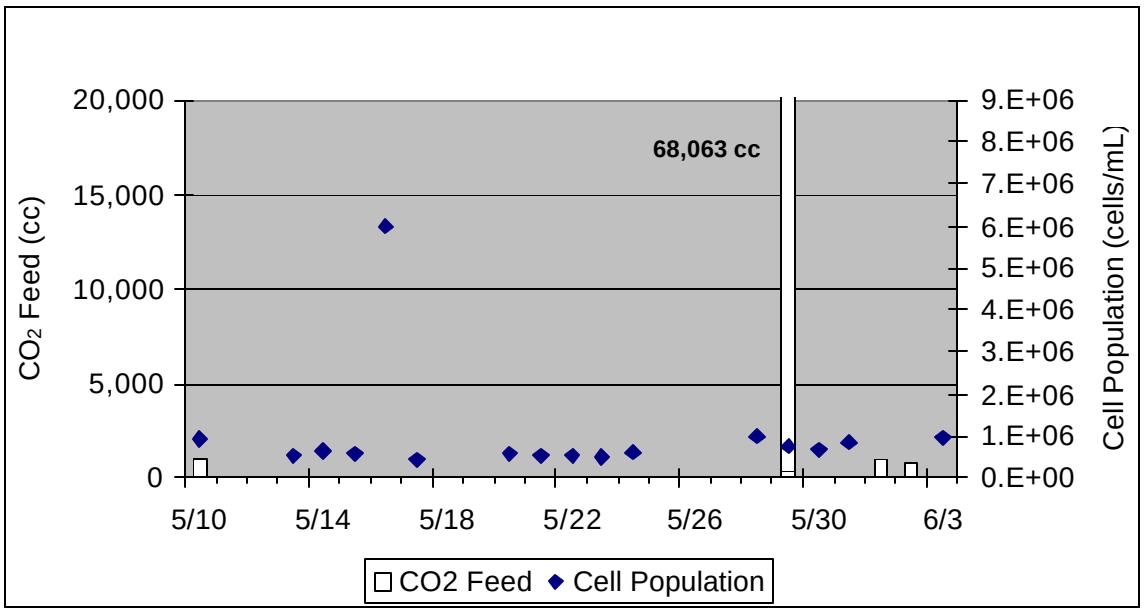


Figure 19
Experiment 5, pH 8.0–8.5

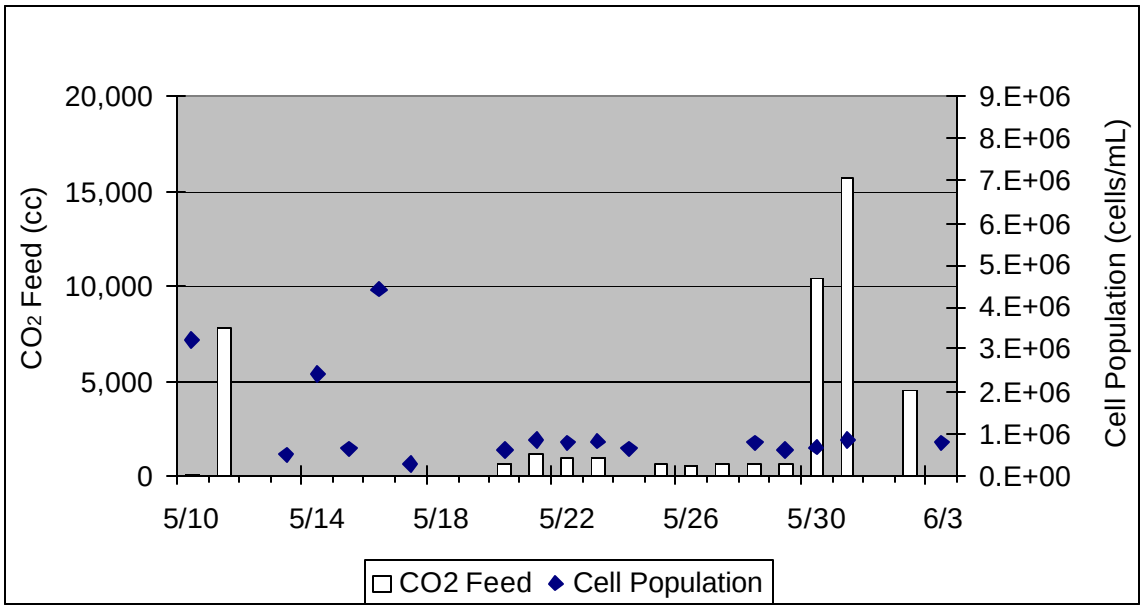


Figure 20
Experiment 5, pH 7.5–8.0

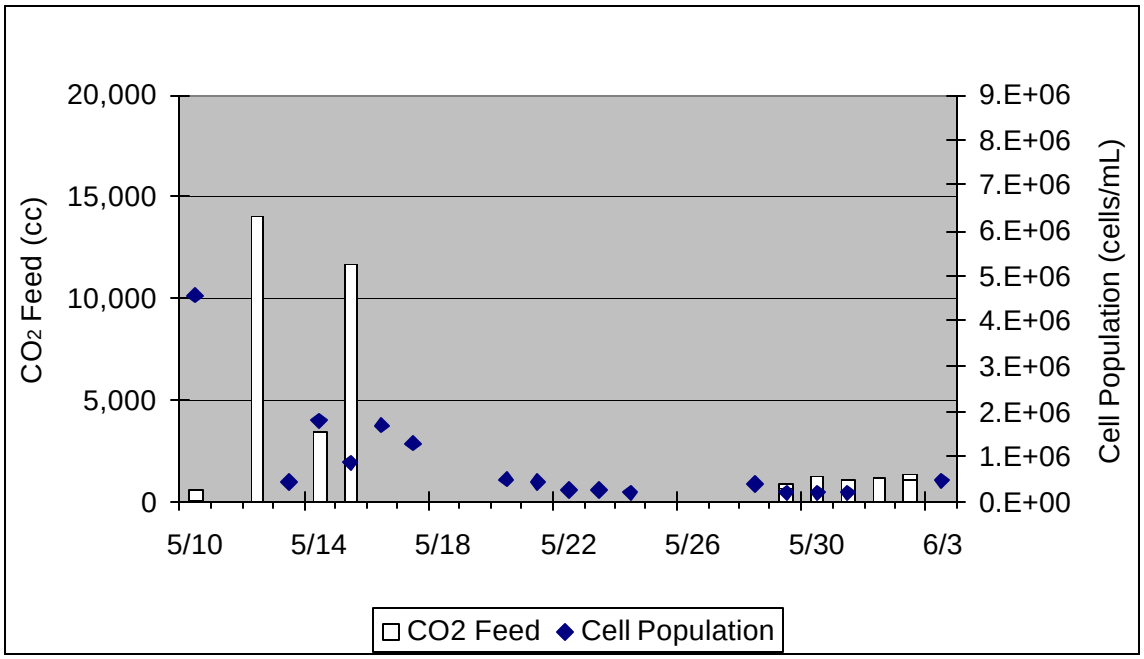


Figure 21
Experiment 5, Control Cell Population

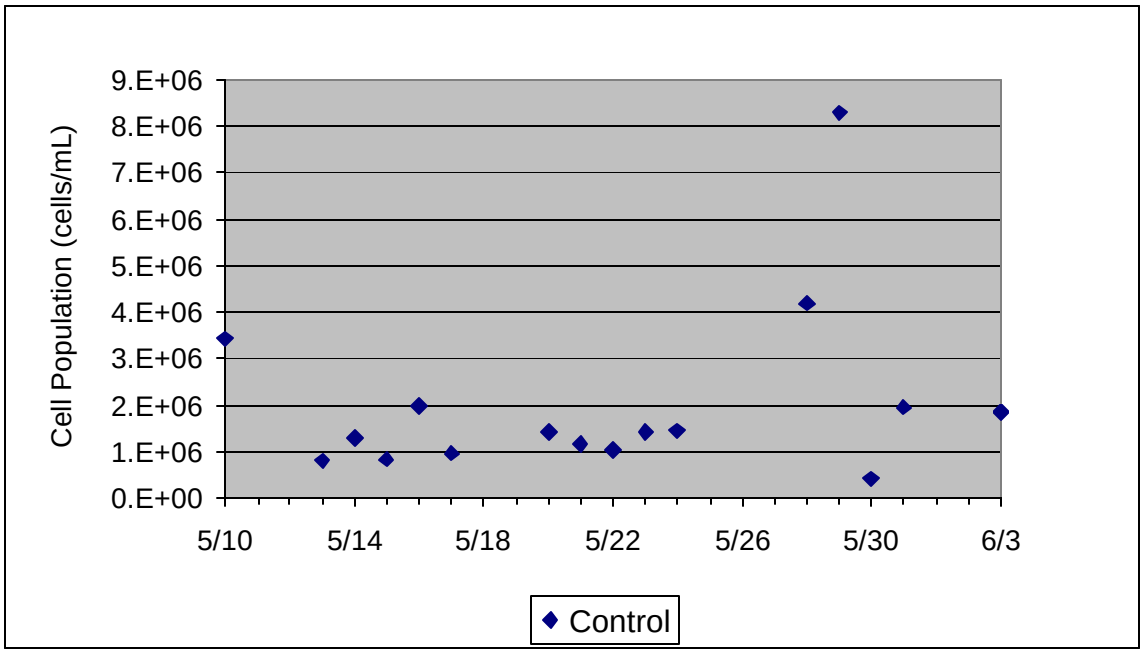


Table 5
Total Biomass Harvested From
Aquariums for Experiment 5

pH Treatment	Total Biomass (g)
9.0–9.5	6.89
8.5–9.0	9.54
8.0–8.5	11.35
7.5–8.0	7.65
Control	13.75

9.0 Conclusions

The amount of CO_2 added to the algal culture solution through the column reactor can be used to control the pH of the growth media. However, the protocol for CO_2 addition appears to affect the growth rate of the algae as much or more than the pH range used to grow the algae. Results indicate that relatively large additions of CO_2 that decrease the pH by as much as one pH unit, followed by a period of no CO_2 addition in which the pH may then increase as much as one unit, may be more effective for producing biomass than maintaining a narrow pH range of 0.2 or 0.5 units. This also simplifies the control process by reducing the amount of control needed to maintain a narrow pH range. The mechanical buffeting of the algal cells by continuous circulation through the pump and reactor column must also be eliminated, since this appears to significantly affect biomass

production. A process that will harvest the cells from the algal culture that have passed through the pump and reactor column, so that only undamaged cells will be in the biomass-producing culture, will be developed for future experiments.